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METHOD FOR SEPARATING MIXTURES OF
POLYOLEFINIC PLASTIC MATERIALS

BACKGROUND

Field of the Invention

[0001] The invention concerns a method for separating plastic material mixtures. The invention is particularly useful for the separation of plastic material mixtures from consumer waste recycling systems, such as the *Dualen System Deutschland* (*Der grüne Punkt*) [The Dual System Germany (The Green Dot System)], in other words, of post-consumer plastic material waste mixtures.

Background of the Invention

[0002] US patent number 5,198,471 describes a method by which polymers are separated from a physical batch of different solid plastic materials. The batch is suspended in a solution-heating vessel in a solvent at a first low temperature at which a first plastic material type dissolves while the other plastic material types remain solid. After a certain dissolving period, the resulting solution is extracted from the heating vessel. New solvent is added which will be at a temperature that will dissolve the next plastic material type in the batch. In this manner, these solution steps are continued until all types of plastic material have been dissolved. Finally, the plastic material types are recovered from each separated solution using the conventional flash evaporation technique. The dissolving period for this process is at least one hour for each dissolving cycle but neither heating periods nor solution removal periods are mentioned in this patent. Usually, these periods, at a minimum, fall within the same time frame.

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[0003] This means that when implementing this prior art process in an industrial setting, if the plastic material batch contain 3 types of plastic material, the throughput of a separation heating vessel would only be 1/3 that of the heating vessel in which the plastic material batch would dissolve 100% right away.

[0004] Furthermore, this prior method has the disadvantage that each plastic material component requires a large interim storage tank so the plastic material preparation can continually drain at the end of the process.

[0005] Furthermore, this prior method has the disadvantage that as the different solutions are removed from the solvent reactor (heating vessel), a relatively large amount of solution remains, an amount which will be larger the finer the plastic material batch has been grinded (to shorten dissolving times). This remaining solution contains dissolved plastic material from the plastic material type previously dissolved and pollutes the subsequent plastic material solutions and therefore the plastic material type. To avoid this disadvantage the remaining batch must be washed with new solvent, which has the disadvantage that it takes more time and requires an additional solvent preparation.

[0006] Additionally, this prior art process has the disadvantage that when removing solution from the first solutions, the solution always also contains fine-grained solid plastic material parts from the not yet dissolved plastic material types, which, when using a flash evaporation technique in the preparation step, inevitably appear as impurities in the newly generated plastic material unless, prior to subsequent processing, an intermediary solution filtration occurs. In an industrial setting, in order to avoid further impurities a separate filtration step would have to be set up for each

plastic material type in the batch, in other words for each solution type. The solid matter generated would have to be returned as suspension to the solvent heating vessel with solvent.

[0007] It becomes clear that when implementing the method described in US patent 5,198,471 in an industrial setting, the investments necessary would become very expensive and that for these reasons, no implementation into an actual industrial installation has occurred.

[0008] EP 0 790 277 A1 describes a polymer separation method in which the plastic material batches are consecutively suspended in different solvents such as toluene, THF, xylene and ethylene benzene at room temperature or, as the case may be, at 135° C to dissolve the plastic material types PS, PVC and polyolefin and to recover each of them. In this manner, the plastic material is recovered from the solution using precipitation with methanol. To recover each polyolefin component, the batch is not dissolved in xylene only at 135° C but also at temperatures of 75° C (LDPE dissolving temperature), 105° C (remaining LDPE and HDPE) and 118° C (PP dissolving temperature). This process has the disadvantage, in addition to the ones already described above with respect to patent US-A-5,198,471, that the different solvents within the same facility will come into contact with parts of the facility and therefore an industrial implementation of the process would require an expensive solvent preparation.

[0009] With all the described methods of the prior art, when a polyolefin batch composed of LDPE, HDPE and PP is used as the starting material, the result will

polymers be recovered from the solution by lowering the temperature and using precipitation/crystallization and the correct precipitation temperature is chosen, most of the wax, polymer chain fragments and additives remain in the solution; however, a smaller undetermined amount is precipitated with the polymer.

[0015] Furthermore, a serious quality issue arises when simply lowering the temperature since the polymer will be precipitated in a fine powder form so that the final filtration of the filter cake will contain approximately 50% to 60% residual moisture.

[0016] This high level of residual moisture contains the undesirable additives mentioned above in proportional amounts, which adversely affects the quality of the polymer blend. The polymer mixture recovered from plastic material waste has the additional problem that the cracked coloring agents from packaging could be concentrated in the polymer phase involved. In the case of a polyolefin mixture, these accumulate during the first phase separation step in the polyethylene-rich phase while the polypropylene phase remains relatively clean; during the second step – during the separation of LDPE and HDPE – they concentrate in the HDPE rich phase.

SUMMARY OF THE INVENTION

[0017] Therefore, it is the purpose of the invention to identify a method that will avoid the above-described disadvantages when recovering polymers from a multi-type plastic material batch. It is the goal to recover polymer blends with a purity level higher than 95%, preferably higher than 97%, using starting material that consists of non-compatible plastic material type mixtures (for example PP and HDPE). Other objectives include:

- The recovery of polymer blends with the lowest possible wax and additive content which stems from the used starting material;
- The recovery of polymer blends with proportions of plastic material types that are highly reproducible, in order to safeguard constant technological characteristics; and
- The simplest technology with a high yield.

[0018] As described below, the method of the present invention achieves these objectives. The invention suggests a method for the separation of mixed plastic materials using a starting material that consists of a polyolefin plastic fraction or another plastic material mixture. The starting material is brought into contact with a solvent, and the temperature of the solution and preferably also the proportion of solvent to volume of plastic material is adjusted in such a manner that at least one of the polymer types and preferably several of the polymer types from the plastic material batch dissolve and the solution as a whole has sufficiently low viscosity for the final solid-liquid separation. The dissolving temperature for the solvent-plastic material mixture is preferably higher than 100° C, and lies in particular approximately between 120°C and 180°C. Finally, at least the single dissolved polymer type is sheared and precipitated from the solution to separate the polymer type from all other components in the solution, including the additional types of polymers contained in the solution.

[0019] To separate each polymer type, the solution passes through one or multiple precipitation steps. Each precipitation step could include several cooling steps to cool the solution to a transportation temperature at which no polymer will be precipitated and finally, to cool the solution in the next or, as the case may be, last, cooling step,

to a precipitation temperature at which each specific polymer type is sheared and precipitated.

[0020] Preferably, the solution is passed through as many precipitation steps as it contains dissolved polymer types whereby, in each precipitation step, the solvent is broken down into to a polymer type as well as the solvent with the remaining dissolved polymer types, polymer fragments, waxes, additives, coloring agents and insoluble materials.

[0021] Analysis of the method according to the invention has revealed that a particularly good separation of the components from a plastic material mixture and particularly clean end products are achieved if, in a first precipitation step, two polymer types together, namely polypropylene and HD-PE are sheared and precipitated, the HD-PE/PP fibers are separated from the remaining LD-PE solution using solid-liquid separation and, finally, the LD-PE, on the one hand, is recovered in the conventional manner from the LD-PE and the PP and HD-PP fibers, on the other hand, are separated in the conventional manner.

[0022] In this, as well as in other embodiments of the invention, one or more of the shearing and precipitation steps of the entire process could be replaced by a separation step for one or more of the polymer types to be separated. In the replacement step(s), a separation of the polymer types in question occurs in the liquid phase taking advantage of a lack of miscibility. In a method similar to the method described in patent application number 198 06 355.5 as seen above, for example, two liquid phases are formed, each of which contains an elevated concentration of different polymer types and these liquid phases are separated in a separating funnel,

centrifuge or a coalescence separator in which, in accordance with the invention, the resulting separated liquid polymer blend solution could be prepared in an additional shearing and precipitation step or shearing crystallization.

[0023] This alternative embodiment in which a precipitation step for a specific polymer type is replaced by a separation step by the formation of several liquid phases, can be technically advantageous as is described in further detail below.

[0024] Even though the shearing and precipitation of polymers from solution to produce fiber structures is basically well known in the prior art (as shown in, for example, patent DE-A-196 18 330) this method has never yet been used for the separation of several polymer types from a plastic material mixture and in particular, from a plastic material waste mixture. However, the invention has surprisingly shown that the separation of polymers using shearing and precipitation yields a fiber structure, which has very low residual moisture and a high level of purity that is superior to the products generated using the conventional methods.

[0025] Preferably, the solution is thoroughly cleaned of inorganic contaminants, additives, coloring agents, undissolved plastic material and the like prior to the separation of the dissolved polymer types in a single or a multiple stepped mechanical solid-liquid separation system. After the separation of the different polymer types, each polymer type is cleaned again as a polymer blend in corresponding washing steps using a solid-liquid separation technique and is recovered using, for example, sequential degassing extrusion or vacuum drying with sequential extrusion. The low molecular weight polymer fragments and the waxes dissolved in the solvent are

recovered from the solution in a separate solvent preparation system using distillation and could be settled as wax using conventional preparation methods.

[0026] The invention also includes a product which is made from a polymer type generated by the method of the invention. The polymer type has a purity of $\geq 90\%$, preferably $>95\%$, and the insoluble or difficult to dissolve foreign polymers contained within this polymer type represent less than 3%, preferably less than 1% of the content. For example, a polypropylene blend generated by the method of the invention has a PP content of more than 90% by weight, preferably more than 95% by weight PP, less than 0.5% PET and PS, preferably a non detectable PET or, as the case may be, PS content, no more than 10% by weight PE content, preferably less than 5% by weight PE, of which the largest share is LDPE. A polypropylene blend in generated in by the method of the invention has the following mechanical characteristics:

Yield stress (ISO 527-1/2) ≥ 30 Mpa

Stretching Elongation (ISO 527-1/2) $\geq 8\%$

E modulus (ISO 527-1/2) ≥ 1000 , preferably approximately 1400 Mpa; and

Charpy impact resistance ≥ 4 Mpa

A PE blend composed of LDPE and HDPE generated by the method of the invention has a composition of at least 97% by weight PE, of which at least 10% by weight is HDPE and at least 10% by weight is LDPE, maximum 3% by weight PP and less than 1%, preferably approximately 0% by weight PS and PET. A HDPE blend generated by the method of the invention has HDPE content of $\geq 95\%$ by weight and a PP content of $\leq 3\%$ by weight, an LDPE content of $\leq 5\%$ by weight and a PET as well as

PS content of less than 1%, preferably approximately 0% by weight. A LDPE blend generated by the method of the invention has an LDPE content of $\geq 95\%$ by weight, a PP content of $\leq 3\%$ by weight, an HDPE content of $\leq 5\%$ by weight and a PET as well as PS content of less than 1%, preferably approximately 0% by weight. A LDPE, HDPE or PP blend generated by the method of the invention has a maximum 5% by weight of the corresponding supplementary polyolefin components, as well as having an added and precipitated fourth polymer component of maximum 20% by weight.

[0027] Other characteristics and advantages of the invention are described in the attached patent claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0028] The invention is described in further detail below with reference to best modes and to the drawings. The Figures show:

- Fig. 1 a schematic representation of an apparatus for the implementation of the method in accordance with the invention;
- Fig. 2 a close-up representation of a possible embodiment of a shearing head which could be used in the apparatus shown in Figure 1;
- Fig. 3 an alternative embodiment of a shearing head which could be used in the apparatus shown in Figure 1;
- Fig. 4 a schematic representation of an additional embodiment of an apparatus for the implementation of the method in accordance with the invention;
- Fig. 5 a flow chart explaining the method in accordance with the invention; and
- Fig. 6 a flow chart explaining a modified embodiment of the method in accordance with the invention; and
- Fig. 7 a flow chart explaining yet another embodiment of the method in accordance with the invention.

Fig. 7 a flow chart explaining yet another embodiment of the method in accordance with the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0029] The method in accordance with the invention is described below with reference to the preparation of plastic material mixtures by the Dualen System Deutschland [The Green Dot System Germany], in particular, with reference to the separation of the polyolefin portion of the mixed plastic material fraction. However, the invention is equally applicable to other kinds of plastic material mixtures.

[0030] The polyolefin share of the Dualen System Deutschland [The Green Dot System Germany] mixed plastic material consists of in total approximately 20 to 30% polypropylene and approximately 35 to 55% LDPE and HDPE from packaging in changing proportions. Of that amount, between 15 and 35 wt. % is HDPE and between 10 and 35 wt. % is LDPE.

[0031] A preferred embodiment of the invention is shown in Figure 5. In the method in accordance with the invention, a sequence of operations of which is schematically shown in Figure 5, a mixture of PP, LDPE, LLDPE and HDPE is used as starting material, as shown in step 10. This starting material is put into contact with a solvent, such as petroleum spirits or n-hexane, and is completely dissolved at an elevated temperature, for example approximately 140° C, as shown in step 12. Instead of petroleum spirits or n-hexane, decalin or xylene could also be used as a solvent. An advantageous value for the adjustment of the polymer concentration in the solvent is approximately 20%. Finally, the solution is cleaned of undissolved compounds in one or several steps using filtration, centrifuging or other mechanical separation techniques, as shown in step 14. In this particular case, when used plastic material

packaging is employed, the insoluble compounds are usually inorganic contaminants, undissolved cellulose parts, PVC, PET or PS packaging materials, paper fibers, non-polyolefin packaging and inorganic filling and the like. Following this mechanical cleaning step, the solution consists 99% or more of the solvent and the dissolved polyolefin plastic materials PP, HDPE, LDPE and LLDPE (hereafter collectively called LDPE).

[0032] In accordance with the first embodiment of the invention shown in Figure 5, each polymer type is precipitated one after the other from the solution using crystallization under simultaneous shearing action to separate each polymer type and to keep waxes, polymer chain fragments and as many coloring agents and filling materials as possible in the solution. Additionally, the solution cleaned in step 14 is sheared and precipitated consecutively at three different temperatures, which are established empirically. In a first precipitation step shown in step 16, the solution is cooled to a temperature T1 and HDPE is sheared and precipitated. In a solid-liquid separation step, the HDPE is separated from the solution so that the fibrous precipitated HDPE, on the one hand, and the remaining HDPE solution on the other hand, will be available separately for the next processing steps as shown in to step 18.

[0033] The fibrous, precipitated HDPE is degassed in a bypass extruder in step 20 so that in step 22 a polymer blend with an HDPE content of 95% and a PP content of $\leq 3\%$ will result.

[0034] The suspension remaining following the separation of the HDPE is cooled to a second lower precipitation temperature T2 to shear and precipitate PP, as shown in step 24. In step 26, similarly to step 18, the solution containing the precipitated PP

fibers, is exposed to a solid-liquid separation to receive the PP fibers, on the one hand, and the remaining suspension, from which the PP was filtered, on the other hand, as shown in step 26.

[0035] The precipitated PP is again degassed in a bypass extruder, as shown in step 28, so a polymer blend with a PP content of 95% and an HDPE content of $\leq 3\%$ will result, as shown in step 30.

[0036] The suspension remaining following the separation of the PP is then cooled in a third step to a third even lower temperature T3 to shear and precipitate the LDPE, as shown in step 32. The solution with the precipitated LDPE undergoes a solid-liquid separation, as shown in step 34 and the recovered LDPE fibers are degassed in a bypass extruder, as shown in step 36, whereby a polymer blend results that contains approximately 95% LDPE. The remaining solvent is reprocessed to clean it of waxes, additives and other impurities in step 40.

[0037] Figure 5 shows the essential features of the invention, the characteristics of which could be modified and adjusted in numerous ways.

[0038] When shearing and precipitating it must be considered that the choice of solvent to be used and the shearing rate will strongly influence the exact precipitation temperature of each polymer type. It should be noted that the precipitation temperatures for the different polymer types must be sufficiently different to ensure definite separation of the different polymer. In the case of the polyolefin plastic material fraction consisting of LDPE, HDPE and PP, it was surprisingly discovered that a separation method using crystallization and simultaneous shearing provides a better separation of the plastic fractions into each different component than the

selective dissolving method from the above mentioned patent number US-A-5,198,471, as can easily be inferred from the table below:

Solvent	Dissolving temperature in method according to patent number US 5,198,471(° C)			Precipitation temperature in method according to the invention (° C)		
	LDPE	HDPE	PP	LDPE	HDPE	PP
Petroleum spirits	70-75	96-103		67-70	95-100	78-86
Decalin	80-90	115-130	130-140	50-60	90-100	70-80
N-hexane	>100	>100	>100	70-80	100-110	80-110

[0039] It is clear from the table above that the temperature ranges for dissolving HDPE and PP overlap in the selective dissolving method from patent number US-A-5,198,471, so that selective dissolving is virtually impossible. However, the precipitation temperatures for the different polymer types HDPE and PP in the method according to the invention at hand differ by approximately 9 to 10° C while the precipitation temperatures for polymer types PP and LDPE using the same solvents would show a difference of approximately 8 to 9° C.

[0040] Not only does the invention demonstrate that a complete separation of precipitation temperatures for each polymer type is possible at which point a true selective separation of the polymer types can be realized, but in contrast to the dissolving method of the prior art in which the dissolving temperature of PP is higher than the temperature necessary for HDPE, the precipitation temperatures for PP, when using the solvents mentioned here, petroleum spirits and decalin, are lower than the temperature necessary for HDPE. In contrast to the prior art, shearing crystallization in the method in accordance with the invention not only provides a substantially better selective separation of the different polymer types contained in

plastic material mixtures but this separation occurs using completely different temperature ranges and it occurs in a different order than seen in prior art.

[0041] The shearing and precipitation in accordance with the invention yields a polymer powder with a fiber-like structure that could be shaped like shish kebab. This fiber structure, which occurs during crystallization, has the additional advantage that the separated polymer following filtration (solid-liquid separation in steps 18, 26 or, as the case may be, 34) has very low residual moisture, which could even be under 10% by weight. Similar to this low residual moisture, the level of waxes and other additives in the recovered polymer powder is very low, which means that the purity of the recovered polymer powder is high and the level of remaining waxes, additives and the like could be further reduced in simple washes of the polymer powder with pure solvents and filtration of the resulting blend.

[0042] Past experience shows that the amount and type of waxes and other additives present in the plastic material mixture as well as the molecular weight distribution of each polymer type have only little influence on the exact temperature setting and the relationship of each precipitation temperature to the other and thus the sharpness of separation or, as the case may be, clarity with which each polymer type can be separated from each other and recovered. Significant deciding factors are the choice of solvent, the temperature control and the shearing rate as well as distribution.

[0043] A variation of the method in accordance with the invention is schematically represented in the flow chart of Figure 6.

[0044] Basically, as shown in Figure 5, it is possible to precipitate and thus to separate each polymer type one after the other using the sequential shearing and

precipitation steps: due to the contamination of the starting material polymer from different coloring agents, pigments and the like, it would be more advantageous from a processing and technical viewpoint to modify the described process. In an alternative embodiment of the invention as shown in Figure 6 it is therefore suggested that, firstly, the polypropylene is dissolved from the plastic material batch consisting of PP, HDPE and LDPE using another method and only afterwards separate the remaining PE types, LDPE and HDPE using shearing and precipitation. The method described in patent application number 198 06 355.5 is suitable for the initial separation of PP.

[0045] The inventor realizes that when separating the PP phase from the PE phase using solubility gaps at higher temperatures, the coloring agents and pigments accumulate in the PE phase resulting in an almost pure PP phase. Should it not only be necessary to separate each polymer or polyolefin type with highest possible polymer purity from a plastic fraction, but also to remove most coloring agents, pigments and the like with a high level of purity, the modified invention method as shown in Figure 5 with a two-step separation method is suggested.

[0046] In the first step of this method (Figure 6), steps 10 to 14 proceed as described above in connection with Figure 5. In step 42, the solution is adjusted to a temperature that allows a separation phase to occur due to the lack of miscibility that results at a higher temperature. This method is described in further detail in patent application 198 06 355.5, which is hereby incorporated by reference.

[0047] When, for example, the solvent n-hexane is used, the solution, which, for example, could have a polymer concentration of 20% by weight, is heated in step 42

to a temperature higher than 170° C, preferably between 180° C and 210° C. At this temperature, after approximately 40 minutes, a polypropylene-rich phase, which can simply be extracted, settles in the upper part of a separating funnel that is sequenced to follow the dissolving heating vessel, as shown in step 44, whereby the high pressure of the solvent n-hexane contributes the necessary driving force. The extracted PP rich solution or phase contains besides the polymer polypropylene also small amounts of LDPE and HDPE, (a total of approximately 4.7%, when using a plastic material mixture of approximately 51% PP, 43% LDPE and 16% HDPE as the starting material) as well as waxes and other additives (approximately 1.6% when using the above mentioned combination as the starting material). The result in the lower phase when using the same plastic material mixture as the starting material is a polymer blend with approximately 3.2% PP and 37.1% LDPE and HDPE as well as 1.5% waxes and other additives, as shown in step 46.

[0048] This modification of the method in accordance with the invention of the polypropylene rich phase from step 44 is mechanically cleaned using centrifuging, filtration or the like, as shown in step 48, to remove coloring agents and remaining insolubles, as shown in step 50. Preferably, the cleaned polypropylene rich phase is not recovered using a flash evaporation technique and degassing extrusion, as is seen in the prior art, but rather is processed further, in accordance with the invention, using shearing and precipitation so that polymer types still contained in the solution are precipitated as polymer powder with a shish kebab-like fiber structure.

[0049] In the embodiment example shown in Figure 6 the cleaned PP rich phase is, firstly, cooled to the first precipitation temperature T1 to shear and precipitate the

remaining HDPE in the solution, as shown in step 52. The resulting suspension is separated using a solid-liquid separation method in step 54 into HDPE fibers (moisture-containing HDPE), as shown in step 56 and into the PP rich solvent, as shown in step 58.

[0050] The PP rich solution resulting from the solid-liquid separation in step 54 is cooled to a second precipitation temperature T2 at which polypropylene is sheared and precipitated, as shown in step 60. The resulting suspension is again separated in a solid-liquid separation step into its components polypropylene and solvent, as shown in step 62.

[0051] The above described steps 52 to 62 for the separation of HDPE and PP using shearing and precipitation at precipitation temperatures T1 or, as the case may be, T2 essentially corresponds to steps 16 to 26 from the method sequence as shown in Figure 5. The HDPE or, as the case may be, PP fibers resulting from steps 54 or, as the case may be, 62 using the solid-liquid separation are finally degassed in a bypass extruder to remove the residual moisture from the polymer powder as also occurs in the method from Figure 5.

[0052] The polyethylene-rich phase recovered in the phase separation in step 42 is further processed essentially as already described with reference to Figure 5. First, the polyethylene rich phase 46 is once more enriched with solvent to generate approximately a 20% polymer content in the solution. To separate coloring agents, remaining insolubles and the like, the solution generated in step 64 is, with the addition of new solvent, exposed to a subsequent mechanical cleaning, for example a centrifuge in step 66. The cleaned solution is cooled to the first precipitation

temperature T1 in step 68 and HDPE is precipitated using shearing. The suspension with HDPE fibers is separated in step 70 resulting in, on the one hand, HDPE fibers 72 and, on the other hand, a remaining solution which in step 74 is cooled to the third temperature T3 and LDPE is precipitated using shearing. The foregoing steps essentially correspond to steps 16 to 18 as well as step 32 of the process described above in reference to the method described in Figure 5. The LDPE suspension generated using shearing and precipitation in step 74 is subsequently processed as in steps 34 to 40 in Figure 5. Steps 56 or, as the case may be, step 72 from Figure 6 correspond to method sequence steps 20 and 22 in Figure 5. Method step 62 in Figure 6 corresponds to method steps 26 to 30 from Figure 5. In other words, the modified method shown in Figure 6 is essentially identical to the method in Figure 5 except for the fact that the starting solution first is separated into a PP rich phase and an HDPE rich phase.

[0053]

Besides the excellent selectivity of the method in accordance with the invention, it is clear that the separation of different polymer types, in accordance with the method of the invention, keeps the residual moisture of the polymer fibers under 10% while the residual moisture in the prior art is approximately 60% by weight. To increase the purity of the product, the recovered polymer fibers (filter-cake) could be washed with pure solution and dehumidified. Since this is a method found in prior art it will not be described in further detail here. Because of the clearly improved removal of moisture and increased purity of the shearing precipitated polymer achieved with the method in accordance with the invention, the additional washing

step is not necessary, since particularly the recovered polymer blends contain only minimal amounts of foreign polymers.

[0054] The modified method shown in Figure 6, in which in general terms the separation of at least one certain polymer type occurs using phase separation instead of shearing and precipitation, has the additional advantage that most coloring agents and other impurities remain in the PE rich phase in the phase separation, while the PP rich phase essentially is free of such impurities.

[0055] An additional particular aspect of the method in accordance with the invention is that the precipitation crystallization occurs in two steps, initially cooling the solution to the coolest possible, but safe, transportation temperature at which no polymer is precipitated and the shearing and precipitation then occurs at a pre-determined precipitation temperature in order to carry out the separation of the polymer type using as little energy as possible and while precisely adjusting the precipitation temperatures.

[0056] Figure 7 again shows an additional modification of the method according to the invention for the separation of polyolefin plastic material mixtures.

[0057] Although, the results from analysis of the method according to the invention are preliminary, they have shown that at least during shearing and precipitation using a multi-stage impulse counter-flow mixer in a heating vessel (as described in further detail below) at shearing rates that allow the precipitation temperatures of each polymer type HDPE, PP and LDPE to reach correspondingly approximately 100° C, 80° C and 75° C, in accordance with the table above, not all plastic material powder is precipitated under all conditions allowing it to easily be filtered but rather that gels

could form which have a high solvent content and which are difficult to process further. To avoid such gel formation, the shearing rate must be increased at which point the precipitation temperatures of PP and HDPE are so similar that their separation into polymer blends with very high purity (greater or equal to 95%) is difficult to achieve. Therefore, in the case of the gel formation, an alternative separation method in accordance with Figure 7 is suggested and explained in further detail below referring to Figure 7.

[0058] In the embodiment shown in Figure 7, firstly, the plastic starting material, which in particular contains PP, LDPE and HDPE is precipitated, as was the case in the above mentioned implementations in accordance with the invention. In a first mechanical separation step using a filter, decanter, centrifuge or the like, insoluble compounds, heavy materials and the like are separated.

[0059] Then the solution is led through a first precipitation step, as occurred in the implementation in Figure 5, and at a precipitation temperature of approximately 60-70° C polypropylene and HDPE is sheared and precipitated together so that only the LDPE remains dissolved in the solution. In this manner, an LDPE solution containing PP/HDPE fibers is generated which could be separated using a solid-liquid separation.

[0060] The remaining solution which now mainly contains dissolved LDPE can be further processed in the conventional manner to recover the LDPE from it in particular using degassing or shearing crystallization as shown in Figures 5 or 6.

[0061] Finally, the PP and HDPE fibers are also separated as described in, for example, Figures 5 or 6, in other words, for example, using a solid-liquid separation

in accordance with the German patent application number 198 06 355.5 or using shearing crystallization as described above.

[0062] The remaining degassing steps, solvent processing, separation of waxes, solvents, additives and so forth could occur as described above.

[0063] The implementation in Figure 7, as has already been discussed, has the advantage that under all currently known processing conditions the gel formation can be prevented using higher shearing rates whereby the components PP and HDPE that were precipitated together, preferably, are separated using liquid-liquid separation. Additionally, the fibers are dissolved again at approximately 140° C and are finally separated in a centrifuge at approximately 170-200° C.

[0064] The method described is reliable and generates polymer blends with high purity.

[0065] Figure 1 shows a precipitation heating vessel which is suitable for the implementation of the method in accordance with the invention.

[0066] Figure 1 shows the precipitation heating vessel 100 fitted with an agitation device 102 which is implemented as a multi-stage impulse counter-flow mixer, a feeding pipe 104 for solvents and a shearing head 106 that is moved with the aid of a driving shaft 108 and a motor 110. In the precipitation heating vessel 100 is a suspension or solution 112 made up of solvent, polymers, dissolved waxes and polymer fragments as well as impurities. The solution is led to a heat exchanger 114 that is fitted with an inlet and an outlet for the coolant fluid. A second heat exchanger 116 serves to adjust a pre-determined constant temperature in the precipitation heating vessel 100. Preferably, this second heat exchanger 116 is a vapor condenser

with a pressure controlled cooling water volume control with a connection to a vacuum system.

[0067] The processing sequence for the precipitation heating vessel, shown in Figure 1, is described below using as an example the separation of PP from a polypropylene rich solution using petroleum spirits as the solvent. The same configuration could naturally also be used for the separation of every polymer type with every suitable solvent providing that the right combination of parameters, in particular the temperature and the shearing rate is chosen.

[0068] In the example at hand, a polypropylene rich solution with a temperature higher or equal to 170° C is led over the first heat exchanger 114 using petroleum spirits as the solvent and in a first processing step is cooled to a temperature that is somewhat higher than the first precipitation temperature, for example to approximately 130° C so that no plastic material polymer is precipitated which could cause the heat exchanger 114 to clog. The solution cooled to this temperature is transported in the pipe 104 under the suspension liquid gauge 112. In one embodiment, the pipe 104 leads into the lower area of the heating vessel; in another embodiment, it opens into the shearing head 106, resulting in two different implementations of the shearing head in Figures 2 and 3.

[0069] In both Figures, it can be seen that the pipe 104 opens into shearing gap 120 or, as the case may be, 122 of shearing head 106' or, as the case may be, 106''. This shearing gap 120 or, as the case may be, 122 can be conical or flat as shown in Figures 2 and 3. The shearing head 106, 106', 106'' can have a smooth or a structured

surface whereby the surface structure will be knobby to safely transport the precipitated polymer powder out of the gap 120, 122.

[0070] In this two-step process, the solution that has been pre-cooled to approximately 130° C abruptly cools to the set precipitation temperature as it leaves the pipe 104 and enters the precipitation heating vessel 105. For the precipitation crystallization of the polypropylene rich solution using petroleum spirits as the solvent, this precipitation temperature lies between 78° C and 86° C.

[0071] The additional heat that entered the precipitation heating vessel 100 with the solution is led out of the system using vapor condensation in the second heat exchanger 116, assuring that the pre-determined constant temperature for the precipitation crystallization of the desired polymer type is always maintained with adequate precision of about $\pm 2^{\circ}$ C in the precipitation heating vessel even on an industrial scale. This precision is achieved as the heating vessel pressure is used as the reference variable for the temperature adjustment, which in this system is in thermodynamic equilibrium with the liquid temperature. At temperatures, which are below the boiling temperature for the solvent at standard pressure, low pressure evaporation cooling is generated with the help of vacuum pumps.

[0072] If in the feeding pipe 104, enough excess pressure relative to the pressure of the suspension in the precipitation heating vessel 100 can be generated, the shearing in accordance with the invention could also be achieved using a correspondingly shaped valve (not shown) at the end of the pipe 104 so that the solution has the desired shearing rate at entry into the precipitation heating vessel 100. In that case, the shearing head 106 shown in the drawing is not necessary.

[0073] In Figure 1 a suspension outlet 118 is shown through which the suspension with the precipitated polymer type can be removed for the solid-liquid separation.

[0074] Figure 4 shows an additional embodiment of the precipitation heating vessel for implementation of the method in accordance with the invention, in which the corresponding components have the same designation. Basically, the precipitation heating vessel is identical to the precipitation heating vessel in Figure 1, in which the solution feeding through the pipe 104 also has a mixing nozzle 130 and a solid-liquid separation step 132. This alternative embodiment allows a part of the suspension in the precipitation heating vessel 100 to be led to the mixing nozzle 130 via a wet grinder 134 and a pump 136 and to be sheared and mixed in the mixing nozzle 130 with an approximately equal amount of solution that was added via the heat exchanger 114. The advantage of this alternative implementation is described in more detail below.

[0075] A polypropylene rich solution is led to the heat exchanger 114 and cooled there to approximately 114° C and led on to the mixing nozzle 130. An equal amount of suspension from the precipitation heating vessel 100 with a temperature of approximately 78° C is also led to the mixing nozzle 130 so that a mixing temperature of approximately 96° C is generated in the mixing nozzle. Petroleum spirits is used as the solvent. As described above, since HDPE dissolves at temperatures between 95° C to 100° C when using petroleum spirits as the solvent and the mixing nozzle 130 (which also can be a dispersing device) generates a shearing effect, the remaining HDPE is dissolved in the PP rich solution in the mixing nozzle 130 while being sheared and can be separated from the PP rich solution using the solid-liquid

separation step 132 prior to being measured out for precipitation in the precipitation heating vessel 100.

[0076] These measures have several advantages. Firstly, the temperature difference between the suspension in the precipitation heating vessel 100 and suspension led past the heat exchanger 114 can be taken advantage of to separate remaining HDPE from the solution in a preliminary step, namely the mixing nozzle 130. Additionally, the resulting repeated pre-cooling of the solution prior to reaching the precipitation heating vessel 100, additionally, help keep the temperature constant in the precipitation heating vessel 100 since the differences in temperatures to be equalized are smaller.

[0077] In the precipitation heating vessel itself 100 the temperature is easily kept constant within $\pm 2^{\circ}$ C of the lowest precipitation temperature of 78° C for PP via the second heat exchanger 116 using vapor condensing. The excess heat can be cooled using the condensation cooling water.

[0078] In the embodiment shown in Figure 4, the desired shearing can be set in the precipitation heating vessel 100 using multi-stage impulse counter-flow mixing blades 138. The suspension generated in the precipitation heating vessel 100 is either led back to the mixing nozzle 130 via the wet grinder 134 and the pump 136 or via the suspension outlet 140 to a solid-liquid separation step. The invention characteristics disclosed above and in the drawings as well as in the patent claims could be significant both individually and in any chosen combination for the different embodiments of the invention.

[0079]

The abbreviations used in Figure 4 have the following meanings:

- MD mixing nozzle for suspension pump volume with pre-cooled solution for shearing and crystallization
- 116 Vapor condenser with pressure led cooling water volume control with connection to a vacuum system.
- M Mixing drive
- MIG Multi-stage impulse counter-flow mixer
- St Flow grinder
- S Controller
- NM1 Wet grinders or, as the case may be, dispersing devices
- P1 Pump
- P2 Speed controlled suspension pump
- TIC Temperature Indication and Controlling
- PIC Pressure Indication and Controlling
- FIC Flow Rate Indication and Controlling
- LIC Level Indication and Controlling
- TCRI Temperature Controlling, Recording and Indication.

[0080]

The foregoing disclosure of the preferred embodiments of the present invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise forms disclosed. Many variations and modifications of the embodiments described herein will be apparent to one of ordinary skill in the art in light of the above disclosure. The scope of the invention is to be defined only by the claims appended hereto, and by their equivalents.

[0081] Further, in describing representative embodiments of the present invention, the specification may have presented the method and/or process of the present invention as a particular sequence of steps. However, to the extent that the method or process does not rely on the particular order of steps set forth herein, the method or process should not be limited to the particular sequence of steps described. As one of ordinary skill in the art would appreciate, other sequences of steps may be possible. Therefore, the particular order of the steps set forth in the specification should not be construed as limitations on the claims. In addition, the claims directed to the method and/or process of the present invention should not be limited to the performance of their steps in the order written, and one skilled in the art can readily appreciate that the sequences may be varied and still remain within the spirit and scope of the present invention.